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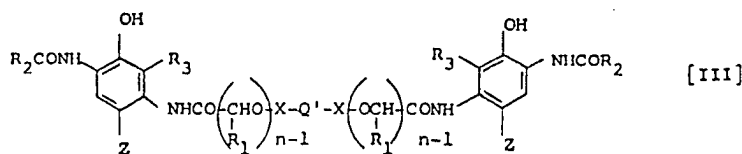
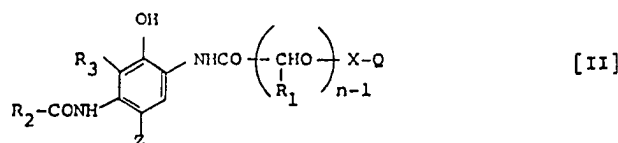
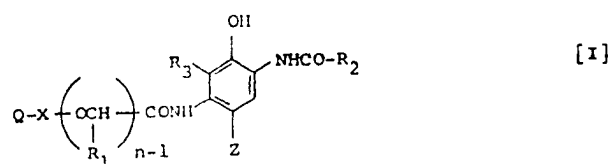
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(12) **UK Patent Application** (19) **GB** (11) **2 070 000 A**

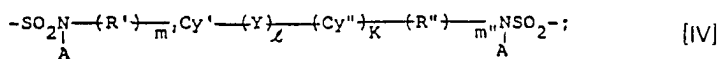
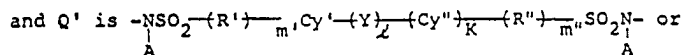
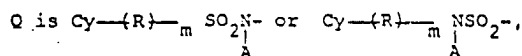
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C8B4G3 C8B4G4 C8B4G5
C8B4G7 C8B4G9 C8B4GX
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 (71) Applicants
Konishiroku Photo
Industry Co. Ltd., No.
26-2 Nishishinjuku 1-
chome Shinjuku-ku,
Tokyo, Japan
 (72) Inventors
Yasushi Usagawa,
Wataru Fijimatsu,
Osamu Sasaki,
Katsumi Matsuura
 (74) Agents
J. A. Kemp & Co., 14
South Square, Gray's Inn,
London WC1R 5EU

(54) **A method for forming a cyan dye image using new 2,5-diacylaminophenol cyan couplers**

(57) A method of forming a cyan dye image is provided which method comprises developing an imagewise exposed silver halide emulsion layer with an aromatic primary amine developing agent in the presence of a cyan coupler represented by the formula [I], [II] or [III]:



wherein, R_1 is a hydrogen atom, or an alkyl radical having 1 to 20 carbon atoms; R_2 is an alkyl, aryl, or heterocyclic radical, R_3 is a hydrogen or halogen atom; X is an arylene or alkylene radical; Z is a split off group; and n is 1 or 2;



wherein Cy, Cy' and Cy'' are individually a cyclic aliphatic, aromatic or heterocyclic group; R, R' and R'' are individually an aliphatic radical; A is a hydrogen atom or a monovalent organic group, Y is a divalent organic group, K, L, m, m', m'' are individually 0 or 1 with proviso that when m=0, Cy is a cyclic aliphatic or heterocyclic group.

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SPECIFICATION

A method for forming a cyan dye image

The present invention relates to a method of forming a cyan dye image, particularly to forming a cyan dye image by color developing a silver halide photosensitive material for color photographic use in the presence of a 2,5-diacylamino type cyan coupler. Further, the invention relates to a method of forming a cyan dye image in the presence of a cyan coupler, which possesses better solubility, dispersion stability and spectral absorption characteristics, and has both a superior dye forming speed and color density especially when developed in a color developing solution which does not contain benzyl alcohol, and has, in addition, superior image preserving properties.

As is generally known, an aromatic primary amine color developing agent reduces exposed silver halide grains such that the oxidized product couples with a coupler. As for cyan couplers to form cyan dyes, the compounds having phenol or naphthol hydroxyl groups are generally used.

The fundamental properties required for couplers include simple dye formation and also good solubility in high boiling organic solvents and alkalis as well as good dispersibility and stability to silver halide photographic emulsions. The dyes formed thereby should have good resistance to light, heat, humidity, etc. The spectral absorption characteristics should be good; there should also be good transparency and color density. Further the image obtained should be sharp. Especially with cyan couplers, there is a need to improve the image preserving properties such as heat resistance, humidity resistance and light resistance.

Further, in view of the anti-pollution measures, it is becoming important to eliminate benzyl alcohol which is used with conventional color developers. However, in general the color developability, viz, the dye forming speed and the maximum color density, of a coupler added to a silver halide photographic emulsion is lowered when benzyl alcohol is absent. Such a tendency is particularly marked with cyan couplers.

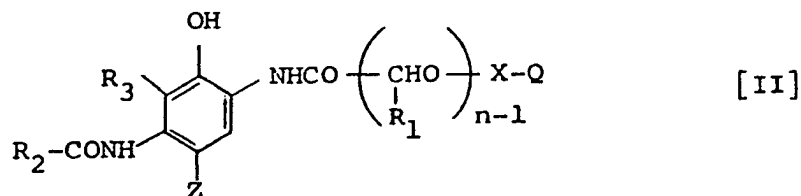
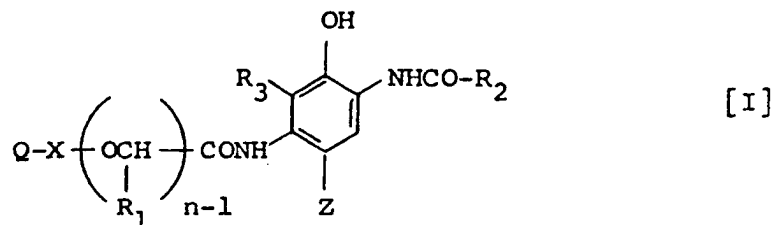
U.S. Patent No. 2,801,171 discloses 6-[α -(2,4-di-tert-amylphenoxy)butaneamido]-2,4-di-chloro-3-methyl phenol, which has been used as a cyan coupler commercially in photographic materials on a large scale, and has excellent characteristics as regards light resistance, but has poor heat resistance and, in addition, its dependence on benzyl alcohol in color developability is high, and the maximum color density is not sufficient when developed in color developer not containing benzyl alcohol.

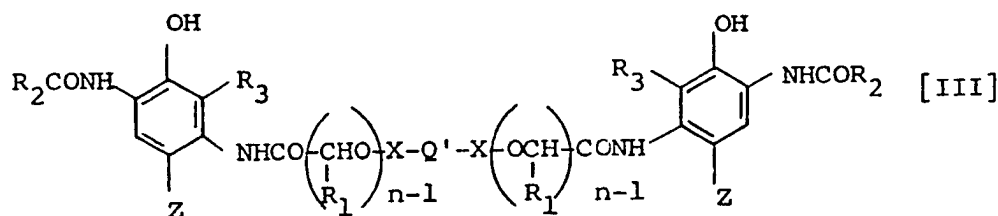
The cyan coupler described in the U.S. Patent No. 4,124,396, is one in which the dicarbonylamino group is substituted in the 2 and 5-positions of the phenol ring; the publication indicates that the dispersion stability at the time of coating or the finish of coating is improved by including a p-alkylsulfonylamino group or p-alkylaminosulfonylphenoxy group as a substituent in the 5-position; however as is obvious from the examples given below, there is a great dependence upon benzyl alcohol in color developability.

It is an object of the present invention to provide a cyan coupler having superior solubility in alkali or a high boiling organic solvent, and dispersibility and stability in silver halide emulsions for color photographic use.

It is a further object of the invention to provide a method of forming a cyan dye image having superior image preservabilities, viz, superior resistance to heat, light and humidity, and, further having a high dye forming speed as well as giving a cyan dye image having great color density when developed in a color developer not containing benzyl alcohol.

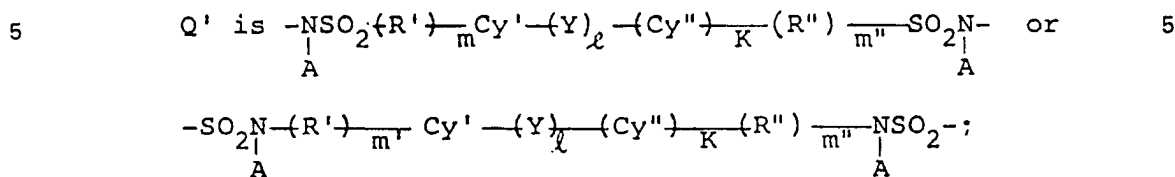
The present invention provides a method of forming a cyan dye image which comprises developing an imagewise exposed silver halide emulsion layer, generally coated on a support, with an aromatic primary amine developing agent in the presence of a cyan coupler represented by the following formula [I], [II] or [III]:





wherein, R₁ is hydrogen atom, or alkyl having 1 to 20 carbon atoms; R₂ is alkyl, aryl, or heterocyclic; R₃ is hydrogen, or halogen; X is arylene or alkylene; Z is coupling off (split-off) group; n is 1 or 2;

Q is $\text{Cy}(\text{R})\text{SO}_2\text{N}(\text{A})$ or $\text{Cy}(\text{R})\text{NSO}_2(\text{A})$, and



wherein Cy, Cy' and Cy'' are individually selected from a cyclic aliphatic, aromatic or heterocyclic group; R, R' and R'' are individually alkyl; A is hydrogen, or a monovalent organic group, Y is a divalent organic group, K, l, m, m', m'' are individually 0 or 1 with proviso that when m=0, Cy is a cyclic aliphatic or heterocyclic group.

10 In a preferred embodiment of the present invention R₁ is hydrogen or alkyl having 1 to 20 carbon atoms; specific examples of said alkyl groups include the methyl group, ethyl group, butyl group and dodecyl group.

Specific examples of R₂ include, as alkyl, methyl, ethyl, isopropyl, butyl, ter-butyl, dodecyl, pentadecyl, and cyclohexyl; as aryl, phenyl, naphthyl; and as a hetero ring having oxygen, nitrogen or sulfur furan. Further, R₂ may have a substituent such as a halogen atom, nitro, hydroxy, carboxy, amino, 15 sulfo, cyano, alkoxy, aryloxy, arylthio, acylamino, carbamoyl, ester, acyl, acyloxy, sulfonamide, sulfamoyl, sulfonyl and sulfoxy oxysulfonyl.

X is preferably methylene, ethylene or terbutylene, or phenylene, naphthylene; among these p-phenylene is most preferable. Each of these groups may be substituted with halogen, alkyl groups such as methyl, ethyl, isobutyl, dodecyl, ter-amyl, cyclohexyl and pentadecyl, nitro, hydroxy, carboxy, amino, 20 sulfo, a heterocyclic group, alkoxy, aryloxy, arylthio, acylamino, carbamoyl, ester, acyl, acyloxy, sulfonamide, sulfamoyl, sulfonyl or morpholino, for example.

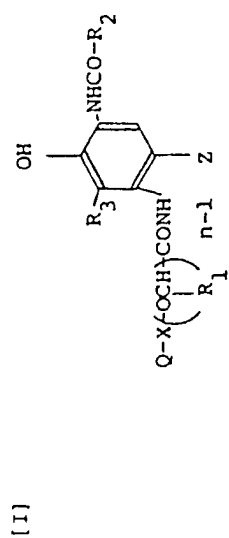
Cy, Cy' and Cy'' are cyclic groups and are preferably 3 to 6 membered aliphatic cyclic groups such as cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl, or cyclooctyl, cyclohexenyl (for Cy) or 25 cyclohexylene (for Cy' or Cy''), or an aromatic group such as phenyl, naphthyl (for Cy) or phenylene (for Cy' or Cy'') or a 3 to 6 membered heterocyclic group containing nitrogen, oxygen or sulfur such as imidazolidinyl, morpholinyl, piperazinyl, pyridyl, or quinolyl. Suitable substituents of these cyclic groups include a halogen atom, nitro, hydroxy, carboxyl, amino, substituted amino, sulfo, alkyl, alkenyl, aryl, a heterocyclic group, alkoxy, aryloxy, arylthio, arylazo, acylamino, carbamoyl, ester, acyl, acyloxy, 30 sulfonamide, sulfamoyl, sulfonyl or morpholino.

R, R' and R'' in Q and Q' are aliphatic groups and they may be either saturated (alkyl) or unsaturated and may further be either straight chained or branched chained, and preferably have 1 to 20 carbon atoms. Examples include methylene, ethylene, trimethylene, propylene, dodecamethylene and propylene group. l is preferably 0.

35 Z is a coupling off group which is well known to the skilled in the art; examples include hydrogen, halogen, aryloxy, carbamoyloxy, carbamoyl methoxy, acyloxy, alkyloxy, sulfonamido, succinimide, the oxygen atom or nitrogen atom being the coupling atom; further concrete examples, which are useful, are given in U.S. Patent No. 3,471,563, the Japanese Patent P.P.I. Publication No. 37425/1972, the Japanese Patent Publication No. 36894/1973, the Japanese Patent O.P.I. Publication Nos. 10135/1975, 40 117422/1975, 130441/1975, 108841/1976, 120334/1975, 18315/1977, 52423/1978, 105226/1978, etc.

A is typically hydrogen, alkyl, aralkyl or phenyl.

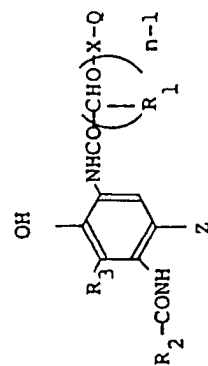
Specific examples of the couplers of the invention are as follows:

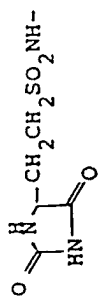
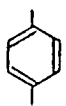
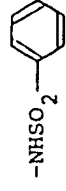
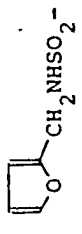
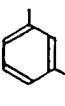
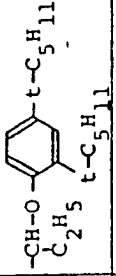

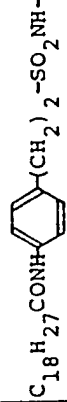
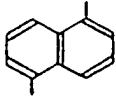
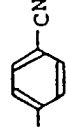
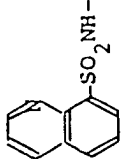
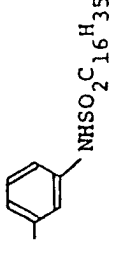

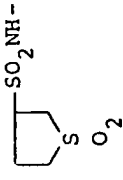
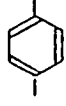
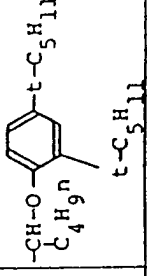
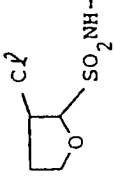
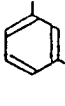
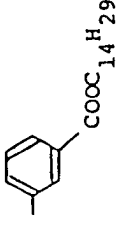


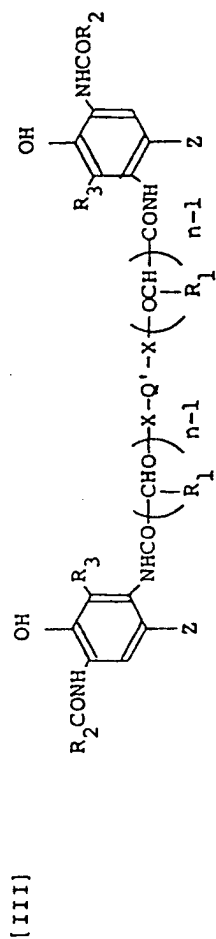
Com- pler No.	Q	X	R ₂	R ₃	R ₁	n	Z
1				H	-C ₁₂ H ₂₅	2	H
2				H	-C ₁₄ H ₂₉	2	Cl
3				H	-C ₂ H ₅	2	-OCH ₂ COOCH ₃
4				H	-C ₁₂ H ₂₅	2	

Cou- pler No.	Q	X	R ₂	R ₃	R ₁	n	Z
5				H	H	2	H
6				H	-C ₁₂ H ₂₅	2	
7				H	H	2	
8			-C ₃ F ₇	H	-C ₁₄ H ₂₉	2	H

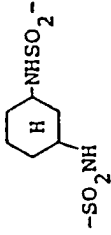


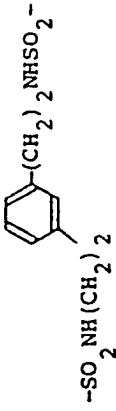


[II]



Cou- pler No.	Q	X	R ₂	R ₃	R ₁	n	Z
9			$-\text{C}(\text{CH}_3)_3$	H	$-\text{C}_{12}\text{H}_{25}$	2	
10				H	—	1	
11				$\text{c}\ell$	H	2	$\text{c}\ell$
12		$-(\text{CH}_2)_3-$		H	—	1	
13				H	—	1	H
14				H	$-\text{C}_4\text{H}_9$	2	$\text{c}\ell$



Cou- pler No.	Q'	X	R ₂	R ₃	R ₁	n	Z
15				H	-C ₄ H ₉	2	Cl
16				H	-C ₁₂ H ₂₅	2	H
17				H	-C ₂ H ₅	2	-OCOOC ₂ H ₅
18				H	—	1	H

Cou- pler No.	Q'	X	R ₂	R ₃	R ₁	n	Z
19				H	-C ₁₂ H ₂₅	2	Cl
20				H	H	2	H

The cyan couplers used in the present invention can easily be synthesized. U.S. Patent No. 4,124,396 discloses a method for synthesis which may be used for the cyan couplers of the present invention.

The following examples are given as typical syntheses of the couplers of the invention:

- 5 *Synthesis Example of Coupler No. 1* 5
- (a) Synthesis of ethyl- α -(m-benzylsulfonylamino-phenoxy) tetradecanoate (intermediate A).
Ethyl- α -(m-aminophenoxy) tetradecanoate (7.3 g) which had been prepared by making use of the method described in the Japanese Patent. O.P.I. Publication No. 109630/1978 and 1.9 g of pyridine were dissolved in 60 ml of tetrahydrofuran and they were stirred together at the room temperature, and then 20 ml of tetrahydrofuran solution (4.2 g) of benzylsulfonylchloride were dropped therein. After 10 stirring under reflux for three hours, the mixture was poured in a solution of 200 ml of ice water containing 12 ml of hydrochloric acid conc., extracted with ethyl acetate, concentrated, after washing and drying, and the residue processed on a column, and 6.2 g (60%) of brown colored oil was obtained. The constitution thereof has been confirmed by means of NMR. 10
- (b) Synthesis of α -(m-benzylsulfonylamino-phenoxy) tetradecanoic acid (intermediate B) 15
The intermediate A (5.2 g) which had been prepared in example (a) was dissolved in 25 ml of ethanol and then 20 ml of ethanol solution containing 2.0 g of potassium hydroxide was added. After reacting for three hours, the mixture was poured in ice water containing 40 ml of 1N-HCl, and after extraction with ethyl acetate and washing and drying, 4.9 g (100%) of brown colored oil was obtained. 15
- (c) Synthesis of α -(m-benzylsulfonylamino-phenoxy) tetradecanoic chloride (intermediate C). 20
The intermediate B (4.9 g) which had been prepared in example (b) was dissolved in 50 ml of benzene and stirred at the room temperature, and 7 ml of thionyl chloride was then added. After stirring under reflux for three hours and concentration 5.1 g (100%) of brown oil was obtained. 20
- (d) Synthesis of illustrated coupler No. 1 25
2-Benzoylamino-5-aminophenol (2.3 g) was dissolved in 30 ml of ethyl acetate and stirred under reflux, and then an ethyl acetate solution of 5.1 g of the intermediate C, which had been prepared in example (c), was dropped therein. After stirring under reflux for two hours, the mixture was poured in water and an organic layer was separated therefrom. After washing and drying, it was concentrated, and a brown residue was obtained. The residue was recrystallized from methanol and then 4.2 g (60%) 25 of white powder was obtained. Melting point thereof was 140—142°C. 30

Elemental analysis

	C (%)	H (%)	N (%)
Theoretical value	68.64	7.06	6.00
Measured value	68.70	7.02	6.12

- 35 The couplers of the invention include the oil-soluble and alkali-soluble of which the oil-soluble couplers are so-called oil-protect type couplers and may be dissolved in an organic solvent having a high boiling point and then may be dispersed in color emulsions. The alkali-soluble couplers may be dispersed in color emulsions by applying Fischer's dispersing method, an example of which is the afore- 35 described sample coupler (6). The resulting color emulsion can be coated on an appropriate photographic support. 40
- Among couplers of the present invention, oil protect type couplers, for example, may be incorporated in color emulsions by a conventional method. For example, after dissolving the coupler of the present invention independently or in combination in a single or mixed liquid comprising an organic solvent with boiling point of more than 175°C such as tricresylphosphate and dibutylphthalate, and a 45 solvent with a low boiling point such as butylacetate and butyl propionate, it is possible to mix it with aqueous gelatin solution containing surface active agent and to prepare a silver halide emulsion by adding it to silver halide after emulsifying with a high speed rotation mixer or a colloid mill. 45
- Various applications of the couplers of the present invention are possible depending on the nucleus and split-off group. In the case where the coupler residual group is one having diffusibility, for example a substituted water-soluble group such as substituted sulfonic acid group or carbocyclic acid 50 group, or when the split-off group is diffusible the coupler of the present invention can be used as a diffusible coupler; for example it can be used for the so-called coupler-in-developer type. Thus in this case, the coupler can be used in the color developer. An example is illustrated coupler 7. 50
- Further, when the coupler of the present invention is one with a non-diffusible cyan coupler, 55 residual group and with a split-off group that is diffusible, it is suitable for use in the diffusion transfer process. In order to give diffusibility to each group, one should select a group with low molecular weight, for example, and/or to induce a water-soluble group such as aforesaid sulfonic acid group for example, and in order to give non-diffusing properties to the group, one should induce long chain 55

aliphatic hydrocarbon residual group and/or select a relatively high molecular group.

This diffusion transfer process uses an image forming method utilizing the cyan dye obtained by the reaction of cyan coupler residual group and color developing agent and an image forming method utilizing the split-off group part which is split off when color developing; an image forming method can be applied to the latter case — the compound obtained with the splitting off of the split-off group from the active point of the coupler needs to be diffusive. If this split off compound is to be used, it needs to be colored and it is necessary, for example, that the dye portion of an azo dye is contained in the compound. This dye portion preferably is one having a water-soluble group; azo dye, azomethine dye, indoaniline dye, indophenol dye and anthraquinone dye are typical. As the coupler of the present invention that is most suitable for use in the diffusion transfer process, illustrated coupler (6) can be mentioned.

As silver halide used for the silver halide emulsion that is useable in the present invention, any silver halide which can be used for ordinary silver halide emulsion such as silver bromide, silver chloride, silver iodobromide, silver chlorobromide and silver chloriodobromide can be used.

Further, it is possible to make a silver halide emulsion of the present invention containing various known photographic additives.

As a spectral sensitizing dye used advantageously in the present invention, cyanine dyes, merocyanine dyes or compound cyanine dyes as described in U.S. Patent Nos. 2,269,234; 2,270,378; 2,442,710; 2,454,629; 2,776,280, for example, are given.

Color developers that can be used for the present invention are preferably those containing an aromatic primary amine group color developing agent as the principal ingredient. Specific examples of this color developing agent include p-phenylenediamine type agents, for example diethyl-p-phenylenediamine hydrochloric acid salt and mono-methyl-p-phenylenediamine hydrochloric acid salt, dimethyl-p-phenylenediamine hydrochloric acid salt, 2-amino-5-diethyl-aminotoluene hydrochloric acid salt, 2-amino-5-(N-ethyl-N-dodecylamino)-toluene, 2-amino-5-(N-ethyl-N- β -methanesulfone-amidoethyl)-aminotoluene sulfuric acid salt, 4-(N-ethyl-N- β -methane sulfoneamidoethylamino)aniline, 4-(N-ethyl-N- β -hydroxy ethylamino) aniline and 2-amino-5-(N-ethyl-N- β -methoxy-ethyl)-aminotoluene.

Such a color developing agent can be used alone or in combination or together with a black-and-white developing agent such as hydroquinone, if necessary. Further, the color developer generally contains an alkaline agent such as sodium hydroxide, ammonium hydroxide, sodium carbonate, sodium sulfate or sodium sulfite and may contain various additives such as alkaline metal halide and potassium bromide.

In the color developing method for the present invention, color development can be achieved by the ordinary coupler in emulsion type color developing process after the photosensitive material is exposed. This color developer is contained in the image receiving material in certain types of diffusion transfer process; in such technology, it is possible to separate the color developing agent from the alkaline agent and to process with other liquid containing alkaline agents or color developing agents when developing if the alkaline agent alone or color developing agent alone is contained in the image receiving material.

As color developing liquid for the aforesaid coupler-in-emulsion type, the one with the following composition can be given as a typical example.

(Composition of color developer)

	4-amino-3-methyl-N-ethyl-N-(β -methane sulfoneamidoethyl)-aniline sulfuric acid salt	5.0 g	
45	Sodium sulfite (anhvdr.)	2.0 g	45
	Sodium carbonate (1 hydrate)	50 g	
	Potassium bromide	1.0 g	
	Potassium hydroxide	0.55 g	
	Add water to make	1 l	

The coupler of the present invention contained in the color emulsion to be used for the present invention reacts with the oxidation product of the color developing agent which is produced when silver halide is developed by such color developer and forms cyan dye.

After the processing with such color development, ordinary photographic processing involving an appropriate combination of processing liquids such as a stop solution containing organic acid, a stop/fix solution containing organic acid and hypo or ammonium thiosulfate, a fixing solution containing hypo or ammonium thiosulfate, a bleaching liquid containing a ferric salt of an aminopolycarboxylic acid and alkali halide, a bleaching and fixing solution containing a ferric salt of an aminopolycarboxylic acid and sodium thiosulfate or ammonium thiosulfate and other stabilizing liquids, as well as washing and drying

operations may be carried out.

A typical example of a color developing process wherein the present invention is used for a coupler-in-emulsion type color negative photosensitive material, will be shown.

(Process)			
5	Processing step (33°C)	Processing time	5
	Color development	3 min. 15 sec.	
	Bleaching	6 min. 30 sec.	
	Washing	3 min. 15 sec.	
	Fixing	6 min. 30 sec.	
10	Washing	3 min. 15 sec.	10
	Stabilizing	1 min. 30 sec.	

Composition of each processing liquid that can be used for in the aforesaid process is as follows, for example.

(Composition of color developer)

15	4-amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)-aniline sulfuric acid salt	4.8 g	15
	Sodium sulfite, anhydrous	0.14 g	
20	Hydroxylamine, 1/2 sulfuric acid salt	1.98 g	20
	Sulfuric acid	0.74 mg	
	Potassium carbonate, anhydrous	28.85 g	
	Potassium hydrogen carbonate, anhydrous	3.46 g	
25	Potassium sulfite, anhydrous	5.10 g	25
	Potassium bromide	1.16 g	
	Sodium chloride	0.14 g	
	Nitrilo acetic acid, tri-sodium salt (1 hydrate)	1.20 g	
30	Potassium hydroxide	1.48 g	30
	Add water to make	1 l	

[Composition of bleaching liquid]

	Ammonium ferric ethylenediaminetetra acetate	100 g	
35	Ethylenediaminetetra acetic acid-di-ammonium salt	10 g	35
	Ammonium bromide	150 g	
	Glacial acetic acid	10 mg	
	Add water to made	1 l	

and adjust to pH 6.0 using aqueous ammonia

[Composition of fixing liquid]

	Ammonia thiosulfate	175.0 g	
	Sodium sulfite anhydride	8.6 g	
5	Sodium metasilicate	2.3 g	5
	Add water to make	1 l	

and adjust to pH 6.0 using acetic acid

[Composition of stabilizer]

	Formalin (37% water solution)	1.5 mg	
10	Konidacks (made by Konishiroku Photo Ind. Co., Ltd.)	7.5 mg	10
	Add water to make	1 l	

A typical example of a color developing process wherein the present invention is used for a coupler-in-emulsion type color photographic material, will be shown next.

15	[Process]		15
	Processing step (30°C)	Processing time	
	Color development	3 min. 30 sec.	
	Bleaching and fixing	1 min. 30 sec.	
	Washing	2 min.	
20	Stabilizing	1 min.	20

Composition of each processing liquid that can be used in the aforesaid process is as follows for example.

[Composition of color developer (1)]

25	4-amino-3-methyl-N-ethyl-N-(β -methane sulfoneamidoethyl)-aniline sulfuric acid salt	5.0 g	25
	Sodium hexametaphosphate	2.5 g	
	Sodium sulfite, anhydrous	1.85 g	
	Sodium bromide	1.4 g	
30	Potassium bromide	0.5 g	30
	Borax	39.1 g	
	Add water to make	1 l	

and adjust to pH 10.30 using sodium hydroxide

[Composition of color developer (2)]

	4-amino-3-methyl-N-ethyl-N-(β -methane sulfoneamidoethyl)-aniline sulfuric acid salt	5.0 g	
5	Benzyl alcohol	15.0 ml	5
	Sodium hexametaphosphate	2.5 g	
	Sodium sulfite, anhydrous	1.85 g	
	Sodium bromide	1.4 g	
	Potassium bromide	0.5 g	
10	Borax	39.1 g	10
	Add water to make	1 l	
	and adjust to pH 10.30 using sodium hydroxide		

15 Aforesaid color developer (1) is a composition of color developer containing no benzyl alcohol and color developer (2) is an ordinary color developing liquid to which benzyl alcohol is added. When the present invention is used for a coupler-in-emulsion type color photographic material, aforesaid color developer (1) and (2) can be used but from the view point of anti-pollution, the use of aforesaid color developer (1) is preferred and good photographic characteristics can be obtained with this desirable color developer (1). 15

[Composition of bleaching and fixing liquid]

20	Ammonium ferric ethylenediaminetetra acetate	61.0 g	20
	Ethylenediaminetetra acetic acid 2 ammonium salt	5.0 g	
	Ammonium thiosulfate	124.5 g	
25	Sodium metabisulfite	13.3 g	25
	Sodium sulfite anhydride	2.7 g	
	Add water to make	1 l	

[Composition of stabilizer]

	Glacial acetic acid	20 ml	
30	Add water to make	1 l	30
	and adjust to pH 3.5—4.0 using sodium acetate		

The present invention is further illustrated in the following Examples.

EXAMPLE (1)

35 Couplers of the present invention (shown with the numbers of the aforesaid examples) as shown in Table 1 below and the following comparison couplers [A], [B] and [C] were used; 10 g of each coupler was added to the mixed solution of 2.5 ml of dibutyl phthalate and 20 ml of ethyl acetate and then heated to 60°C and dissolved completely. The solution thus obtained was mixed with 5 ml of 10% aqueous solution of alkanol B (alkyl naphthalene sulfonate, made by E.I. Du Pont de Nemours & Co.) and 200 ml of 5% aqueous solution of gelatin and then emulsified by a colloid mill and a dispersion of 40 each coupler obtained. Then, this coupler dispersion was added to 500 g of gelatin-silver chlorobromide (containing silver bromide of 20 mol%) emulsion and was coated and dried on polyethylene coated paper and 6 samples of silver halide photosensitive material for color photography having stable coated film (sample Nos. (1)—(6)) were obtained. The 6 samples were given a conventional wedge exposure and then, as a concrete example, was given a color development 40

according to the aforesaid coupler-in-emulsion type color developing process and a cyan color image obtained. Two kinds of composition of one containing benzyl alcohol (aforesaid color developer (2)) and the other no benzyl alcohol (aforesaid color developer (1)) were used as color developing liquid. Photographic characteristics were measured for each of the samples obtained. The results thereof are shown in Table 1.

TABLE 1

Sample No.	Coupler used	With benzyl alcohol added		Without benzyl alcohol added		Maximum absorption wavelength (m μ)
		Sensitivity	Maximum density (Dmax)	Sensitivity	Maximum density (Dmax)	
1	Illustrated coupler (1)	100	2.20	80	2.05	643
2	„ (12)	100	2.20	83	2.21	650
3	„ (16)	100	2.20	84	2.20	645
4	Comparison coupler A	100	2.20	55	1.52	655
5	„ B	95	1.91	60	1.55	645
6	„ C	100	1.81	50	1.54	655

In the Table, the values of sensitivity are shown as a relative value against the value of 100 for the sensitivity of sample (4) with benzyl alcohol added wherein comparison coupler [A] is used. The structures of comparison coupler [A], [B] and [C] are as follows.

10 Comparison coupler [A]

6- $[\alpha$ -(2,4-di-tert-amylphenoxy)butane amide]-
2,4-dichloro-3-methylphenol (the one described
in aforesaid U.S. Patent No. 2,801,171)

15 Comparison coupler [B]

2-benzamide-5- $[\alpha$ -(4-butylsulfonyl-aminophenoxy)
tetradecanamide]phenol (the one described in U.S.
Patent No. 4,124,396)

20 Comparison coupler [C]

6- $[\alpha$ -2,4-di-n-amylphenoxy)butaneamide]-2-chloro-
3-methyl-4-(1-phenyl-5-tetrazolyloxy)phenol
(the one described in aforesaid U.S. Patent No.
3,839,044)

As is clear from aforesaid Table 1, samples processed with the image forming method of the present invention have desirable spectral absorption characteristics and further it can be seen that the sensitivity and the maximum density of the color image obtained with color developer having no benzyl alcohol added is greater than for any of the comparison couplers [A], [B] and [C].

EXAMPLE (2)

In the same manner as foregoing example (1), 6 samples (7—12) were obtained and light-resisting properties, heat-resisting properties and humidity-resisting properties thereof were checked. Results obtained are shown on Table 2.

TABLE 2

Sample No.	Coupler used	With benzyl alcohol added			Without benzyl alcohol added		
		Light-resisting property	Heat-resisting property	Humidity-resisting property	Light-resisting property	Heat-resisting property	Humidity-resisting property
7	Illustrated coupler (1)	80	100	98	81	100	98
8	" (9)	92	100	100	91	100	100
9	" (19)	91	100	100	92	100	100
10	Comparison coupler A	91	65	73	90	64	72
11	" B	72	100	98	71	100	97
12	" C	91	65	72	90	65	71

In the table, values of the light-resisting property represent the residual density of each image after exposure by a xenon fade meter for 200 hours with the density before the exposure given as 100. Values of humidity-resisting property represent the residual density after storage for two weeks at 60°C and 80% relative humidity with the density before the test given as 100. Further, values of the heat-resisting property represent the residual density after storage for two weeks at 77°C with the density before the test given as 100.

As evident from Table 2, comparison couplers [A] and [C] have excellent light-resisting properties but they have poor heat-resisting properties. The heat-resisting properties of the comparison coupler [B] are better than those for comparison couplers [A] and [C] but the comparison coupler [B] has poor light-resisting properties.

On the other hand, in the coupler (1), (9) and (19) of the present invention, an improvement in light-resisting properties can be seen even if they are compared with aforesaid comparison coupler [B].

EXAMPLE (3)

10 g of each illustrated coupler (8) of the present invention and aforesaid comparison coupler [A], was added to the mixture of 25 ml of dibutylphthalate and 20 ml of ethylacetate and was heated up to 60°C and was completely dissolved. The solution thus obtained was mixed with 5 ml of 10% aqueous solution of alkanol B and 200 ml of 5% aqueous gelatin solution and was emulsified by a colloid mill to obtain a complex dispersion. Next, this dispersion liquid was added to 500 g of emulsion of high sensitive gelatin silver iodobromide (containing 6.0 mol% of silver iodide) for a negative and then was coated and dried on a cellulose acetate film base; samples 13 and 14 of silver halide photographic photosensitive material having a stable coated film were obtained. This silver halide photographic photosensitive material was exposed in the same manner as example (1) and color developing was conducted according to aforesaid coupler-in-emulsion type color developing process for color negative, and cyan color images were obtained.

Photographic characteristics of cyan color images thus obtained were measured. The results thereof are shown in Table 3.

TABLE 3

Sample No.	Coupler used	Relative sensitivity	Maximum density (Dmax)	Maximum absorption wavelength (λ_{\max})
13	Illustrated (8) coupler	100	2.50	670
14	Comparison A coupler	54	1.54	660

As is evident from table 3, the sample with the coupler of the present invention used therein has a higher maximum density. Also the sample of the present invention provides cyan negative color images with excellent transparency.

EXAMPLE (4)

Aforesaid illustrated coupler (6) that is a coupler of the present invention, was incorporated in an ordinary high sensitive silver iodobromide emulsion for a negative by the Fischer dispersion method (0.2 mol amount was used for 1 mol of silver halide), and this emulsion was coated on the triacetate film base by an ordinary method and then dried.

Samples thus obtained were exposed in the same manner as example (1) and then they were processed for 3 minutes at 24°C with the use of an alkaline developer with the following composition.

[Composition of developing liquid]

Sodium sulfite	20 g
4-N-ethyl-N- β -hydroxyethyl-aminoaniline	11.0 g
Add water to make	1

At the time of this development, the image receiving layer containing dimethyl- β -hydroxyethyl- δ -stearoamidepropyl-ammonium-hydrogenphosphate provided on a polyethylene-coated paper was contacted with the photosensitive layer of the aforesaid sample and after the development, the image

receiving material was peeled off. Thereupon, in the same manner as aforesaid examples (1), (2) and (3), a clear cyan positive image with a high maximum density and excellent photographic characteristics was obtained on the image receiving material; it was thus confirmed that the coupler of the present invention has excellent properties for use as a coupler for the diffusion transfer process.

5 EXAMPLE (5)

Illustrated coupler (7) was dissolved in methanol and added to a color developing liquid to form a coupler in developer type color developing liquid of the following composition:

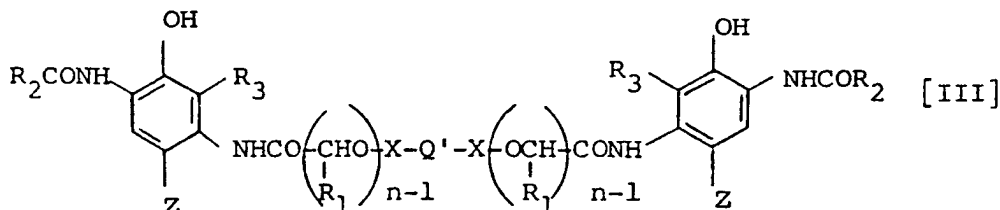
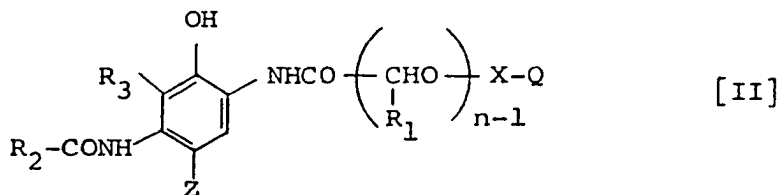
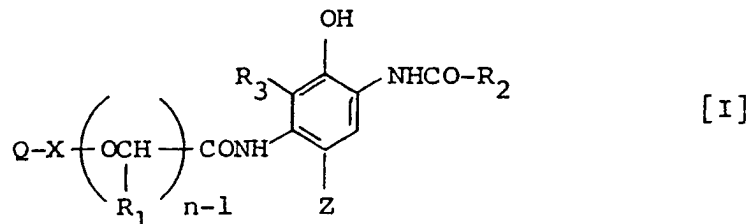
	N,N-diethyl-2-methyl-p-phenylenediamine	2.0 g	
10	Sodium sulfite, anhydrous	2.0 g	10
	Sodium carbonate (monohydrate)	20.0 g	
	Potassium bromide	1.0 g	
	Illustrated coupler (7)	2.0 g	
	Add water to make	1	

15 A sample obtained by coating the high sensitive silver iodobromide emulsion onto a subcoated polyethyleneterephthalate film was exposed in the usual way and then was developed for 3 minutes at 24°C with the aforesaid coupler-in-developer type color developing liquid.

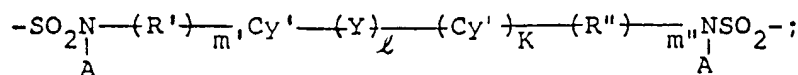
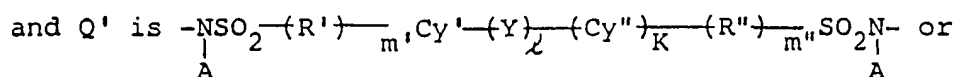
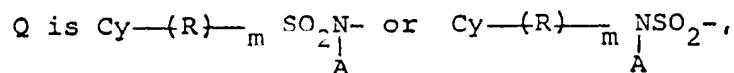
After the development, washing for 4 minutes, bleaching for 5 minutes, washing for 5 minutes, fixing for 5 minutes, washing for 30 minutes and drying were conducted in a conventional manner as a result of which a cyan image with absorption maximum of 665 nm and excellent spectral absorption characteristics and with other excellent photographic characteristics was obtained.

Claims

1. A method of forming a cyan dye image which comprises developing an imagewise exposed silver halide emulsion layer with an aromatic primary amine developing agent in the presence of a cyan coupler represented by the formula [I], [II] or [III]



wherein, R_1 is a hydrogen atom, or an alkyl radical having 1 to 20 carbon atoms; R_2 is an alkyl, aryl, or heterocyclic radical; R_3 is a hydrogen or halogen atom; X is an arylene or alkylene radical; Z is a split off group; and n is 1 or 2;



5. wherein Cy, Cy' and Cy'' are individually a -, clic aliphatic, aromatic or heterocyclic group; R, R' and R'' are individually an aliphatic radical; A is a hydrogen atom, or a monovalent organic group, Y is a divalent organic group, K, l, m, m', m'' are individually 0 or 1 with proviso that when m=0, Cy is a cyclic aliphatic or heterocyclic group. 5
- 10 2. A method according to claim 1, wherein Cy, Cy' and Cy'' are individually a 3 to 6 membered cyclic aliphatic radical, a 3 to 6 membered heterocyclic radical containing a ring nitrogen, oxygen or sulphur atom, or an aromatic group. 10
3. A method according to claim 1 or 2 wherein A is hydrogen.
4. A method according to any one of the preceding claims, wherein X is a p-phenylene group.
- 15 5. A method according to any one of claims 1 to 4, wherein the cyan coupler is one represented by the formula [I] or [II]. 15
6. A method according to claim 5 wherein the cyan coupler is one represented by the formula [I].
7. A method according to any one of claims 1 to 4, wherein the cyan coupler is one represented by the formula [III].
8. A method according to claim 1 substantially as described in any one of Examples (1) to (5).
- 20 9. A cyan coupler of formula [I], [II] or [III] as defined in any one of claims 1 to 6. 20
10. A color photographic material having a silver halide emulsion layer containing a cyan coupler as defined in any one of claims 1 to 6 coated on a support.
11. An aromatic primary amine color developer which contains a cyan coupler as defined in any one of claims 1 to 6.